

USE OF THE MASS SPECTROMETER IN THE ELUCIDATION OF ORGANOMETALLIC COMPLEX STRUCTURES: STUDY OF TWO NEW CARBONYL CLUSTERS OF COBALT, $\text{SCo}_4(\text{CO})_9[\text{P}(\text{CH}_3)_2]_2$ AND $\text{S}_2\text{Co}_3(\text{CO})_7\text{P}(\text{CH}_3)_2$

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(Received February 3rd, 1972)

SUMMARY

The formation of two new cobalt carbonyl cluster compounds, $\text{SCo}_4(\text{CO})_9[\text{P}(\text{CH}_3)_2]_2$ (I) and $\text{S}_2\text{Co}_3(\text{CO})_7\text{P}(\text{CH}_3)_2$ (II) in the reaction of $\text{Co}_2(\text{CO})_8$ with $(\text{CH}_3)_2\text{P}(\text{S})\text{P}(\text{S})(\text{CH}_3)_2$ is described. Their compositions have been elucidated from their mass spectra, emphasis being laid on the ^{13}C and ^{34}S satellites of the principal peaks. This procedure is discussed in detail, and is recommended for more general use in organometallic chemistry.

INTRODUCTION

Since the appearance of the first papers demonstrating the possibility of studying the organometallic compounds, including metal carbonyls, by mass spectrometry¹⁻³, the usefulness of this type of analysis for unknown organometallic samples has been fully recognized.

Many papers dealing with the preparation of new compounds now report the molecular weight of the sample, obtained from its mass spectrum. However, we would like to draw attention to the fact that the mass spectrum provides additional information, as important as the molecular weight, which is very helpful in the elucidation of the structures of unknown organometallic complexes. This is true even when a low resolution mass spectrometer is used.

As an example of the way of exploiting this technique, we describe a mass spectrometric study of two new compounds⁴ obtained in the reaction of dicobalt octacarbonyl with tetramethylbiphosphine disulphide, $(\text{CH}_3)_2\text{P}(\text{S})\text{P}(\text{S})(\text{CH}_3)_2$. No

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reactions of $\text{Me}_4\text{P}_2\text{S}_2$ with metal carbonyls have been reported previously, although addition compounds with transition metal salts⁵ and cationic nitrosyl derivatives such as $[(\text{NO})_2\text{Co}(\text{S}_2\text{P}_2\text{Me}_4)]\text{Br}$ ⁶ have been described.

EXPERIMENTAL

2.000 g (5.85 mmole) of dicobalt octacarbonyl and 1.088 g (5.85 mmole) of tetramethylbiphosphine disulphide were dissolved in 50 ml of chloroform and allowed to react at room temperature in an inert atmosphere. After 2 days the reaction was considered complete, since no dicobalt octacarbonyl was detectable in the IR spectrum of the mixture. Evaporation of the brown-red solution left a brown residue, which was readily soluble in n-hexane.

In the chromatographic working up of this solution on a silica gel column, we eluted first with n-hexane to obtain a brown fraction of $\text{Co}_4(\text{CO})_{12}$ identified by its IR spectrum. Then we eluted with a mixture of n-hexane and benzene (9/1 in volume), and obtained two more fractions. The first, green, zone gave after crystallization from n-hexane deep green crystals [compound (I)]. (Found: C, 24.53; H, 1.8; Co, 36.3%. Mol.wt. (osmometric), 630.)

The second fraction was red, and gave after evaporation of the eluent and recrystallization from hexane a red solid [compound (II)]. (Found: C, 21.5; H, 1.14; Co, 34.9%. Mol.wt. (osmometric), 505.)

The yields of both compounds (I) and (II) are quite high, their sum being near 70%. Their ratio varied considerably, however, when reaction conditions were changed. In CHCl_3 as solvent the distribution of the products is ~60% of (I) (green) and ~40% of (II) (red), whereas in CH_2Cl_2 solution the reaction is considerably faster and the distribution is ~20% of (I) and ~80% of (II).

The mass spectra were obtained with an Atlas CH4 mass spectrometer. In accordance with previous suggestions⁷, the electron energy was 50 eV, and the trap current 20 or 60 μA . The samples were introduced with a direct insertion probe at the lowest temperature which gave a sufficiently intense spectrum. $\text{W}(\text{CO})_6$ and $\text{Re}_2(\text{CO})_{10}$ were used as standards to calibrate the mass scale. Some peaks which had different intensities relative to those of the molecular ions when samples of different preparative runs were used, or when the temperature of the probe was changed, can be attributed to impurities, and are not reported. For experimental details see ref. 8.

RESULTS

The mass spectrum (Fig. 1) of the green compound (I) showed the following features:

(1). The ion with the highest mass/charge value was found at 642 amu. Assuming that thermal decomposition⁹ was not significant, this indicates a molecular weight of 642.

(2). The molecular ion ($m/e=642$) was followed by two isotopic peaks ($m/e=643$ and 644) having respectively about 15% and 7% of the intensity of the 642 peak. In view of the preparative procedure, the molecule could not contain atoms other than Co, C, O, S, P, and H. In the light of the natural isotopic distribution of these

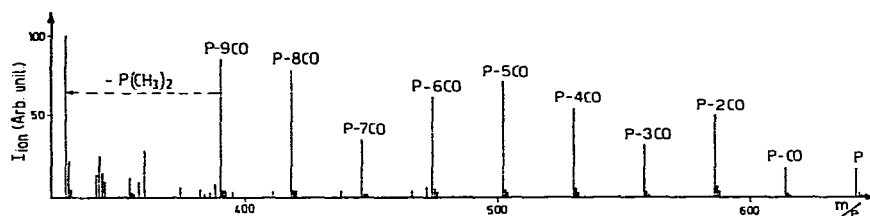


Fig. 1. Mass spectrum of compound (I) obtained from the reaction of $\text{Co}_2(\text{CO})_8$ with $\text{Me}_2\text{P}_2\text{S}_2$. Its formula corresponds to $\text{SCo}_4(\text{CO})_9(\text{PMe}_2)_2$. (A few other ions, generally of low abundance and having m/e values lower than 329 were also observed.)

elements¹⁰, and making the necessary probability calculations¹¹, it is found that the above percentages correspond to a molecule containing 13 carbon atoms, one sulfur, and about 9 oxygen atoms.

(3). Nine intense peaks starting from the molecular ion and spaced by 28 amu were observed. According to the well known characteristics of the fragmentation of metal carbonyl derivatives under electron impact¹², this indicates the presence of 9 carbonyl groups in the molecule.

(4). The $[\text{P}-9\text{CO}]^+$ ion shows two isotopic peaks, one and two amu higher than the main peak. Their percentages in respect of the main peak were 4.9% and 4.2% for the $[(\text{P}-9\text{CO})+1]^+$ and $[(\text{P}-9\text{CO})+2]^+$ ions, respectively, (where P stands for the parent molecular ion) indicating the presence of 4 carbon atoms and again only one sulphur atom. All other $[\text{P}-n\text{CO}]^+$ fragments had these two isotopic satellites, but while the $[(\text{P}-n\text{CO})+2]^+ / [\text{P}-n\text{CO}]^+$ intensity ratio was almost constant, the $[(\text{P}-n\text{CO})+1]^+ / [\text{P}-n\text{CO}]^+$ intensity ratio decreased as n increased. This is in accord with the fact that on increasing n , the number of carbon atoms in the ion decreases, but all the ions contain one sulphur atom.

(5). A strong peak is observed at m/e 329. It is assigned to the species formed by loss of a $\text{P}(\text{CH}_3)_2$ fragment from the $[\text{P}-9\text{CO}]^+$ ion.

Thus we have direct evidence for the presence of 11 carbon atoms (9 from the CO groups and 2 from the dimethylphosphide moiety), whereas from the analysis of the isotopic peaks of the parent ion there is a proof for the presence of 13 carbon atoms. It is thus very likely that there are two more CH_3 groups in the molecule, probably linked to a phosphorus atom to give a second $\text{P}(\text{CH}_3)_2$ moiety. The difference between the mass of the parent ion (642 amu) and that of $9\text{CO} + 2\text{P}(\text{CH}_3)_2 + \text{S}$ (406 amu) corresponds to four cobalt atoms (236 amu).

Hence the molecular formula of compound (I) turns out to be $\text{SCo}_4(\text{CO})_9\text{-}[\text{P}(\text{CH}_3)_2]_2$. This formulation is in agreement also with the elemental analysis and molecular weight data.

The analogous analysis of the mass spectrum (Figs. 2 and 3) of compound (II) shows the following characteristics:

- (1). The molecular weight is 498 amu.
- (2). It contains 2 sulphur and 9 carbon atoms.
- (3). There are 7 carbonyl groups present (involving 7 out of the 9 carbon atoms of the molecule).
- (4). It contains one $\text{P}(\text{CH}_3)_2$ group; this is suggested by a CH_3 , CH_3 , P cascade starting from the $[\text{P}-7\text{CO}]^+$ peak (m/e 287, 272, and 241 respectively).

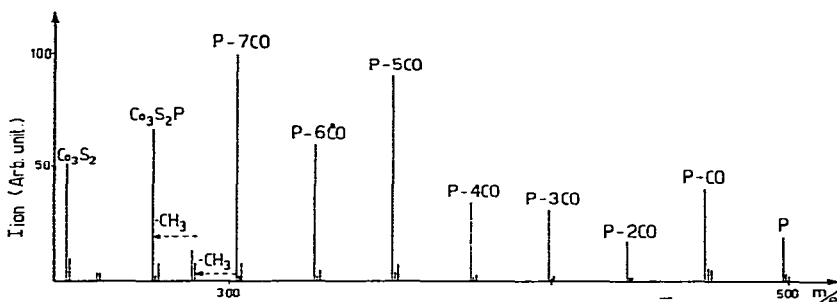


Fig. 2. Mass spectrum of compound (II) obtained from the reaction of $\text{Co}_2(\text{CO})_8$ with $\text{Me}_2\text{P}_2\text{S}_2$. Its formula corresponds to $\text{S}_2\text{Co}_3(\text{CO})_7(\text{PMe}_2)$. (A few other ions, generally of low abundance and having m/e values lower than 241 were also observed.)

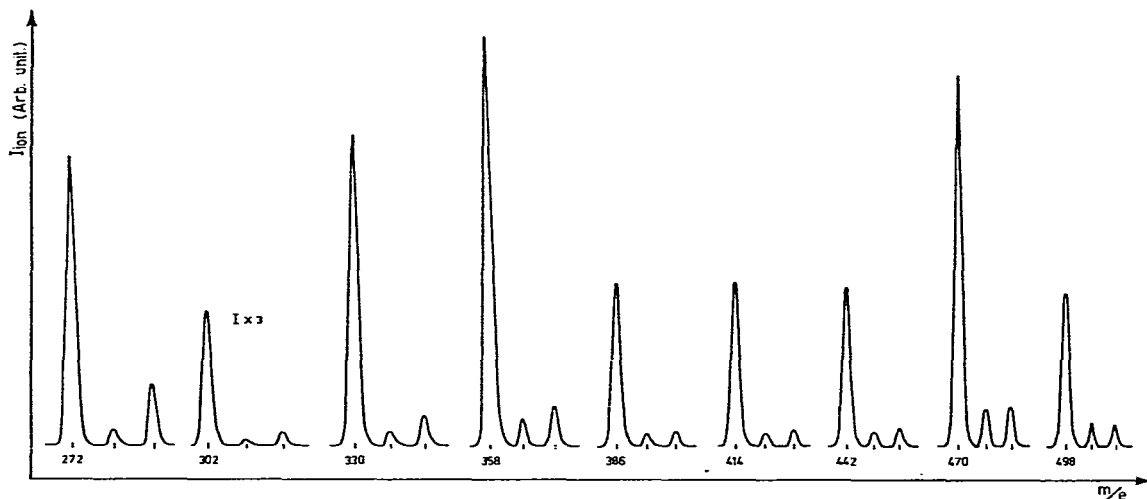


Fig. 3. Isotopic pattern of the various $[\text{P}-n\text{CO}]^+$ ions from compound (II). The $[(\text{P}-n\text{CO}) + 1]^+$ peaks are mainly due to the carbon atoms, while the $[(\text{P}-n\text{CO}) + 2]^+$ peaks are mainly due to the sulphur atoms. The natural isotopic distributions are: ^{12}C 98.9%, ^{13}C 1.1%; ^{32}S 95.0%, ^{33}S 0.75%, and ^{34}S 4.2%.

These facts suggest that the molecular formula of compound (II) is $\text{S}_2\text{Co}_3(\text{CO})_7\text{P}(\text{CH}_3)_2$. Summing the exact atomic masses of the main isotopes of the atoms contained in this formula gives a molecular weight of 497.83 amu. This is in good agreement with the value of the main parent peak (497.82 amu), which was established by using the $\text{Re}_2(\text{CO})_5^+$ and $\text{Re}_2(\text{CO})_4^+$ ions from $\text{Re}_2(\text{CO})_{10}$ (main isotopic peaks at 511.88 and 483.88 amu, respectively) to calibrate the mass scale.

In this case, again, elemental analysis and osmometric molecular weight data agree with the proposed formulation.

DISCUSSION

Our results indicate that we have obtained two compounds of a new type which contain sulphur and dimethylphosphido groups in the same cobalt carbonyl cluster.

In the case of compound (II), of all the conceivable structures we prefer that

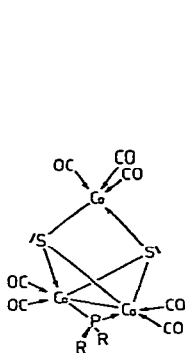


Fig. 4. Proposed structure for $S_2Co_3(CO)_7P(CH_3)_2$ (II).

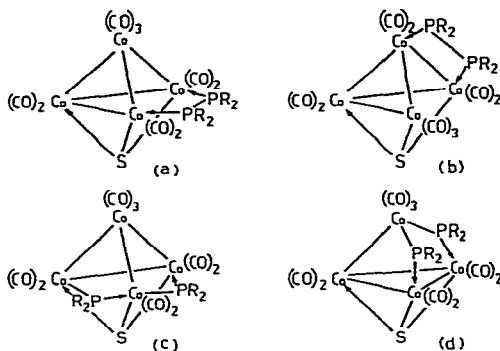


Fig. 5. Possible structures for $SCo_4(CO)_9[P(CH_3)_2]$ (I).

reported in Fig. 4. This structure satisfies the inert gas rule, and is consistent in all respects with the mass spectral fragmentation pattern. Moreover, the infrared spectrum of (II) in the region of the C–O stretching vibrations shows 4 bands and 2 weak shoulders (2086 m, 2046 vs, 2040 s, 2030 (sh), 2025 m, and 2019 (sh) cm^{-1}), which is in acceptable agreement with the selection rules that predict 6 $\nu(CO)$ frequencies for point group C_{2v} (if the perturbing effect of the apical $Co(CO)_3$ group with C_{3v} local symmetry is neglected), or 7 $\nu(CO)$ bands for C_s symmetry.

Unfortunately, it is not so easy to assign a definite structure to compound (I). The main reason for this is that we have no experimental evidence for the absence or the presence of a P–P bond. As is known from results obtained with carbonyls of iron or of the chromium group metals¹³, biphosphines can act as four-electron donors, the P–P bond being retained and linking two $M(CO)_x$ entities, or the P–P bonds splitting to give two R_2P phosphido groups which take up bridging positions and act as three-electron donors.

In Fig. 5 we give some possible structures which satisfy the inert gas rule for all the cobalt atoms. A common feature of these structures is a trigonal bipyramid involving an apical sulphur and an apical cobalt atom, the other three cobalt atoms lying in the equatorial plane. In structures (a) and (b) an unsplit biphosphine bidentate ligand links two equatorial Co atoms (a), or links an equatorial Co atom with the apical one (b). The other two possible structures, (c) and (d), contain two separate dimethylphosphido bridges along two equatorial or two "meridional" edges of the TBP, respectively. In all cases the inert gas rule requires the absence of one direct Co–Co bond for each bridging Me_2P or Me_4P_2 group.

The mass spectral features are not in conflict with any of the proposed structures. In particular, in the spectrum there is a very intense peak at m/e 329 which we think must correspond to a very stable cluster structure, $SCo_4P(CH_3)_2^+$. This is, indeed, the ion of lowest m/e value among those of significant intensity. However, it is not conclusive to decide which one of the four proposed structures is the most probable. Two different fragmentation routes could lead to the same $SCo_4P(CH_3)_2^+$ ion starting from a compound having either structure (a) or (b), or from one having structure (c) or (d). In the first case the P–P bond cleavage might be followed by a $P(CH_3)_2$ elimination and by the formation of a new cluster having a bridging phos-

phido group. In the second case, a $\text{P}(\text{CH}_3)_2$ elimination followed by a linkage of two cobalt atoms would give rise to the same final ion. Unfortunately there is no information in the literature on the fragmentation of $-\text{PMe}_2-\text{Me}_2\text{P}-$ or Me_2P moieties, and so it is impossible to decide between the two types of structures on the basis of mass spectral data.

In the IR spectrum, selection rules predict 9 CO stretching bands for compound (I) either on the basis of a C_s [structures (a), (c), or (d)] or of a C_1 [structure (b)] symmetry, but the observed spectrum shows only five well-resolved bands at 2073 s, 2029 vs, 2003 m, 1988 s, and 1941 ms cm^{-1} . Thus, as in many other cases, the observed number of C–O stretching bands is lower than that predicted, presumably because of coincidences and of near-zero intensities for some bands. Hence even the IR spectrum does not enable a decision to be made between the possible structures.

It is worth noting, however, the large separation (132 cm^{-1}) between the highest and the lowest bands, which indicates considerable differences in the electronic situations of the cobalt atoms. In structures (a) and (c) there is a $\text{Co}(\text{CO})_3$ group which is linked only by Co–Co bonds to the cluster, and is not under the direct influence of the P- or S-ligands, which are known to be worse π -acceptors than CO thus giving a partial negative charge to a metal atom to which they are bonded. In structures (a) and (d) there are two, and in (c) three Co atoms bearing both the phosphinic ligand(s) and the sulphur atom. Although we are aware that the neglect of the interactions between CO groups bonded to different metal atoms of a cluster represents a considerable over-simplification, this effect could be responsible only for a splitting of 20 to 30 cm^{-1} . Taking in account also the effect of the geminal CO–CO interactions, there remains a separation of 60–70 cm^{-1} which must be due to the great (1.0–1.2 mdyne/Å) difference between the force constants of C–O bonds in different environments. Thus it seems logical to suppose that the lower C–O stretching frequencies are mainly due to the $\text{Co}(\text{CO})_2$ groups bonded to S and PMe_2 ligands, whereas the vibrations of the $\text{Co}(\text{CO})_3$ group free from the direct influence of these ligands are concentrated in the highest frequencies. If this reasoning is valid, structures (a) and (c) must be favoured over (b) and (d).

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